Introduction:
An aqueous solution of carbon dioxide produces a mixture of carbonate and bicarbonate ions. Determining the carbonate and bicarbonate ions in each other's presence is often important in environmental chemistry.

1) \( \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq) \)
2) \( \text{H}_2\text{CO}_3(aq) \rightarrow \text{HCO}_3^-(aq) + \text{H}^+(aq) \)
3) \( \text{HCO}_3^-(aq) \rightarrow \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \)

The alkalinity of water is the capacity of solutes to act as a base by reacting with protons. There exists a fundamental difference between the expression of acid-base properties of pH and alkalinity. Whereas the pH can be considered to be an intensity factor which measures the concentration of alkali or acids immediately available for reaction, the alkalinity is a capacity factor which is a measure of the ability of water sample to sustain reaction with added acids (in a sense, it is the ability of a water body to neutralize added acids). In practice, it may be determined by measuring the number of moles of \( \text{H}^+ \) required to neutralize all bases dissolved in one liter of water leaving no further capacity for neutralization of additional protons. We say that alkalinity can be determined by titration of one liter of a water sample to the end point. Acidification of a lake in its natural setting is itself analogous to a macro-scale titration and lakes are sometimes termed well-buffered, transitional, or acidic (strong, intermediate, weak neutralization capacity, respectively) depending on their position on the titration curve.
Alkalinity is therefore a useful measure of the capacity of water to resist acidification from acid addition (e.g. acid precipitation). The presence of carbonate, bicarbonate, and hydroxide ions usually imparts most of the alkalinity of natural or treated waters. Initially, your water samples may contain bases and will contain a positive alkalinity. When all the bases have been used up (beyond the end point), alkalinity is negative and is equal to -[H$^+$].

The addition of acid to the selected seawater sample will convert the carbonate to bicarbonate (reverse of reaction 3) until no carbonate remains. The addition of further acid will convert the bicarbonate to carbonic acid until no more bicarbonate remains (reverse of reaction 2). The carbonate and carbonic acid equivalence points may be determined either by titration using indicators or by pH titration.

The first end point determined (in the pH range 8.3-10) represents the completion (equivalence point or stoichiometric end point) of the following reaction:

$$\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$$

i.e. the carbonate has been neutralized by the acid-forming bicarbonate ions.

In the pH range 3.2-4.5, all of the bicarbonate ions initially present in the water sample, together with all of those produced from the reaction of the carbonate ions, will be neutralized. The resulting alkalinity is known as the total alkalinity.

$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

The importance of the carbonate/bicarbonate system in natural waters stems from its ability to act like a buffer in natural waters. The oceans are described as being buffered since relatively large quantities of acid or base can be added to seawater without causing much change to its pH. However, it is now recognized that the increasing atmospheric concentrations of carbon dioxide, released from anthropogenic activities, are actually "titrating" the world's oceans resulting in reducing ocean pH and carbonate ion concentrations. Experimental evidence suggests that if these trends continue, key marine organisms - such as corals and some plankton - will have difficulty maintaining their external calcium carbonate skeletons. Moreover, many freshwater lakes do not have a large buffer capacity and consequently a small addition of acid (e.g. from acid precipitation or industrial effluent) can cause large changes in pH without warning seriously affecting the biological systems they support. Finally, the carbonate alkalinity and the total alkalinity are useful for the calculations of chemical dosages required in the treatment of natural water supplies.
Alkalinity Titration or using the scientific method to identify an object

**Note:** You will perform this section in small group (3-4) but will do your write-up individually.

**Objectives:** The general goals of this second approach is to learn how to *problem solve* using an instrument, devising a protocol to test a question, and finally verifying your results vs. the initial stated hypothesis (do you have validation? If not, what could have gone wrong?). You are expected to come up with your own protocol and approach, not follow a prescribed menu. It is important that you give room to your creativity or prior knowledge. Make sure that, whatever the results are in the end, you conclude (reflect) on both the scientific results and the performance of this pseudo-scientific exercise.

**Initial questions:** You are provided with a water samples and an estimated value for its alkalinity (140-150 mg total CaCO$_3$ alkalinity per liter), and you need to figure out

a) what is the water sample (seawater, fresh water, tap water, etc)?

b) what type of acid did you used in your titration?

You know that the acid is a 0.01 M solution but do not know if it was initially made from a phosphoric acid (H$_3$PO$_4$), sulfuric acid (H$_2$SO$_4$), or hydrochloric acid (HCl).

You will be answering these questions based on two simple methods: measurement of the pH and alkalinity titration of the water sample.

**Question 1**

State a hypothesis(es) and test protocol(s) to answer the question above.

**Question 2**

Perform the alkalinity titration of the water samples following the protocol below. Save your titration data and enter it in an Excel spreadsheet. Calculate values of total alkalinity in mg of CaCO$_3$ per liter of water (mg/L) using your titration data.

**Question 3**

Based on your results, can you safely state what the acid is? If not, what other information are you missing? Did anything go wrong, and if yes can you still say anything the test you performed?

**Summary of the Method:**

Alkalinity is measured by titrating a water sample with acid (0.01M). The Vernier sensor is used to monitor pH during the titration. The equivalence point will be at a pH of approximately 4.5, but will vary slightly, depending on the chemical composition of the water. The volume of the acid added at the equivalence point of the titration is then used to calculate the alkalinity of the water.
Material checklist:
1) pH sensors
2) 25-50 ml burets
3) 100 ml graduated cylinder
4) 250 ml beakers (2)
5) Wash bottle with DI water
6) Utility clamps & Ring stand
7) 0.01 M unknown acid solution
8) Magnetic stirrer and bar

Procedure: pH Titration
Caution! Please wear gloves and safety goggles to perform this experiment and beware that the acid solution is corrosive. Avoid spilling it on your skin or clothing.
Note: Please make sure you transfer all the measurements (volume, pH) in your notebook to be able to graph the pH change vs. volume later on.

1) Pour 50 ml of water into a beaker.
2) Place the beaker on the base of a magnetic stirrer and drop a stir bar carefully into the beaker. Set the stirrer to a speed that mixes the sample well, but does not splash.
3) Insert the electrodes of the pH meter into the beaker.
4) Ensure complete coverage of the electrodes. It is essential that adequate clearance is achieved between the electrodes and the magnetic stirrer or the stir bar will not rotate.
5) Place the burette (previously filled with 0.01 M acid solution) over the beaker so that acid can drip slowly into the beaker. Ensure that you have sufficient room to turn the tap of the burette freely.
6) You are now ready to perform the titration. This process goes faster if one person manipulates the burette while another person operates the computer and enters volumes.
7) Monitor the pH value on the computer screen. Once it has stabilized, record the value.
8) Add a small quantity of acid titrant (enough to lower the pH about 0.2 units, never more than 1 ml). When the pH stabilizes, record the value.
9) Record the current burette reading to (the nearest 0.1 ml).
10) Continue adding acid solution in increments that lower the pH by about 0.1-0.2 pH units and enter the volume reading after each increment. When the pH values begin to drop more quickly (at approximately 5.5) change to 0.2-0.3 ml increments. Enter a new burette reading after each addition. Note: It is important that all additions of acid in this part of the titration be less than 0.5-1.0 ml.
11) When the pH values start to flatten out (approximately pH 3.8-4.0), again add larger increments that lower the pH by about 0.2 pH units (1 ml), and enter the burette readings after each increment.
12) Continue for two to three more additions, or until the graph clearly shows that the pH has leveled off again.
13) Rinse the pH sensor with DI water from the wash bottle. Use a second beaker to catch the rinse water. Return the sensor to the storage solution bottle and tighten the cap.
14) Enter your data on an Excel spreadsheet and graph it.
15) For a graphical method to determine precisely the end points, plot the change in pH divided by the change in volume for each increment - DpH/Dvol - on the y-axis against the volume of acid added (in that increment) on the x-axis. This is the same as the 1st derivative obtained from the Vernier software.